

# **Geochemistry of Sulfur in Iron Corrosion Scales Found In DW DS**

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# Acknowledgements

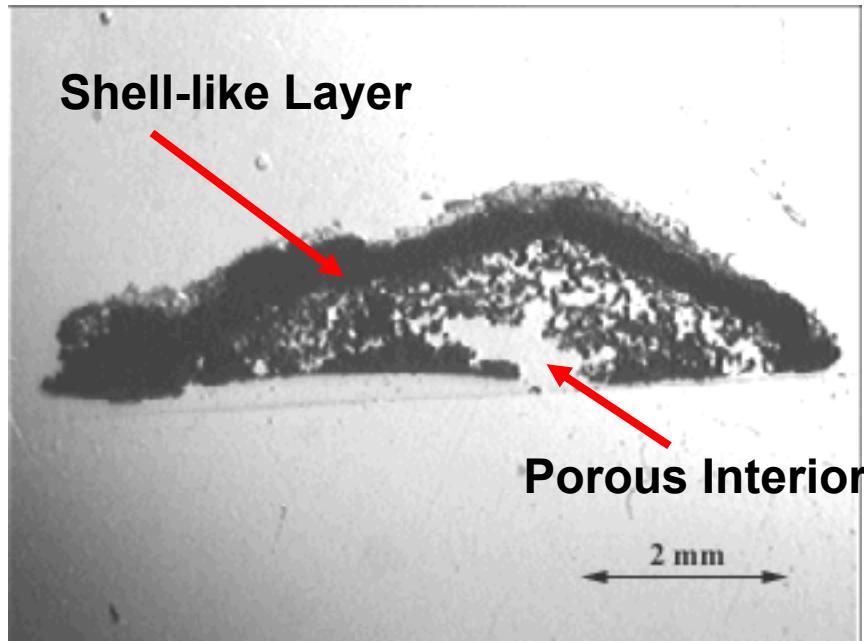
- **Christy Muhlen, Keith Kelty, Barbara Francis, Cliff Johnson, and Mike Schock**
- **Battelle Memorial Institute (Bruce Sass, Abe Chen)**
- **Water Utilities (Cincinnati Water Works)**



# Background

## Typical Scale Structure and Composition

(University Of Illinois, Snoeyink and Sarin)



- Corrosion scales are **porous deposits** with a hard **shell-like layer**
- **Reservoir of Fe(II)** ions exists in the scale interior
- Composition
  - **Shell-like layer:** Magnetite ( $\text{Fe}_3\text{O}_4$ ) and goethite ( $\alpha\text{-FeOOH}$ )
  - **Porous Interior:** Mostly Fe(II) compounds, green rusts (possible), and ???
  - Fe(III) compounds present only in the top layers. Also other solids.



# Research Objectives

Compare the sulfur composition (form, composition, etc..) in iron scales from two drinking water distribution systems-

-chlorinated surface water and low DO ground water



# Test Sites

## Site 1

- Ohio
- Surface water
- Alum  
coagulation/filtration
- Activated carbon
- Well chlorinated

## Site 2

- Michigan
- Ground water
- Multiple wells
- Iron in source water
- Rotten egg odor



# Water Chemistry of Test Sites

Site	Location	pH	DO, mg/L	Cl <sub>2</sub> , mg/L	Ca, mg/L	Fe, mg/L	Mg, mg/L	Na, mg/L	PO <sub>4</sub> , mg/L	SO <sub>4</sub> , mg/L
Utility 1										
	distribution system*	8.48	6.45	0.99	36	--	12	36	--	98
Utility 2										
	well 6 with PO <sub>4</sub> treatment	7.53	--	--	84	0.36	24	73	nd	66
	well 7	7.76	--	--	94	0.64	29	68	nd	81
	well 7 with PO <sub>4</sub> treatment	--	--	--	93	0.63	28	69	7.02	80
	well 9	7.59	1.15	nd	46	nd	18	12	0.23	19
	well 9 with PO <sub>4</sub> treatment	--	--	--	40	0.19	14	17	1.06	13
	well 1	7.41	1.55		115	1.4	44	43	nd	114
	distribution	--	--	0.1-0.2	--	1.22	--	--	--	--



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# Pipe Samples



Site 1



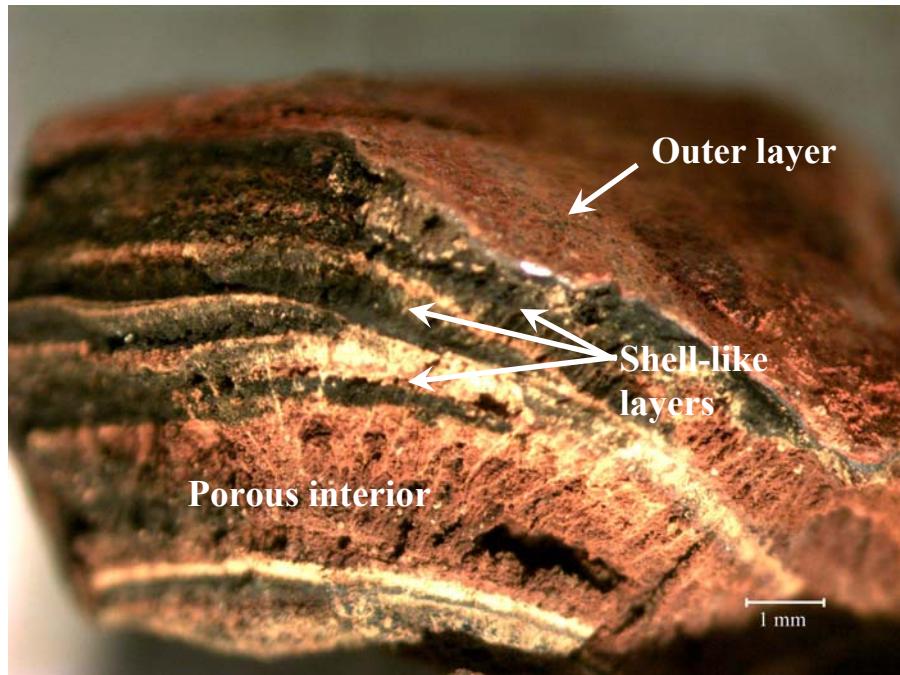
Site 2



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# Pipe Sample- Site 1



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# Pipe Sample- Site 2



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# Elemental Composition of Scale

Sample Number	Sample ID	Mg wt%	Al wt%	Si wt%	P wt%	Ca wt%	Mn wt%	Fe wt%	S wt%
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Utility 1

Site1a	0.011	0.032	0.081	0.099	0.08	0.238	54	1.0
Site1b	0.020	0.132	0.060	0.097	0.72	0.029	58	2.7

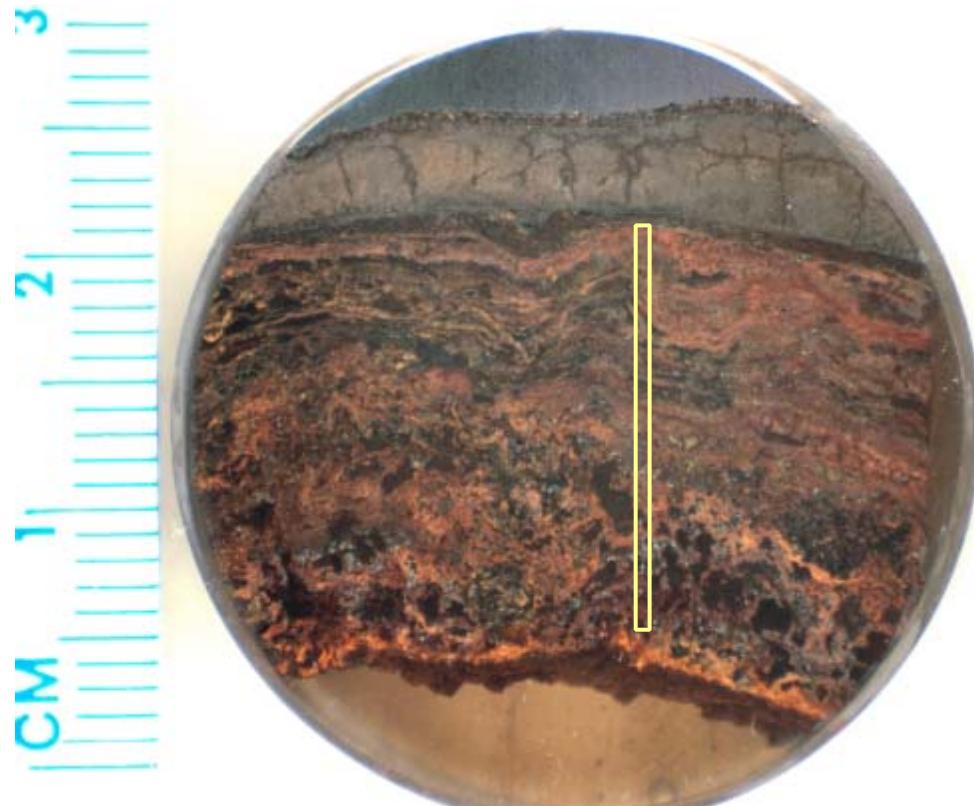
Utility 2

d100038	0.109	0.072	0.196	0.081	2.51	0.180	51	6.5
d100039	0.361	0.139	0.204	0.067	1.77	0.047	43	11.2
d100042	0.040	0.017	0.096	0.250	0.67	0.031	53	15.5
d100046a	0.076	0.012	0.128	0.069	0.78	0.042	53	22.3
d100046b	0.083	0.003	0.197	0.086	4.83	0.086	46	12.9
d100046c	0.050	0.003	0.116	0.049	3.07	0.109	53	8.8
d100046d	0.062	0.013	0.042	0.100	2.27	0.094	52	13.9



# Elemental Mapping

## Site 2



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# Elemental Composition

Site 2

## Cross-sectional Elemental Mapping

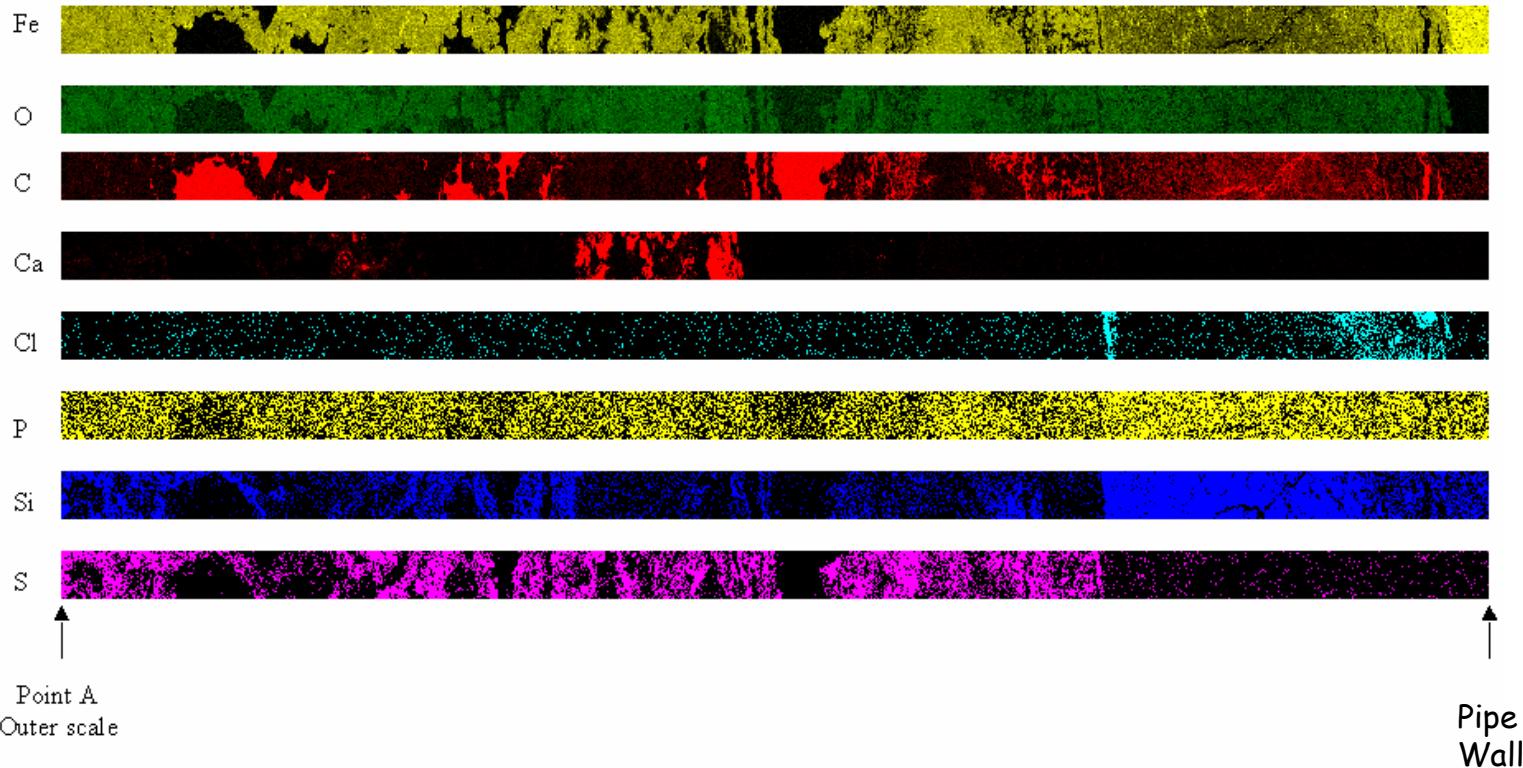
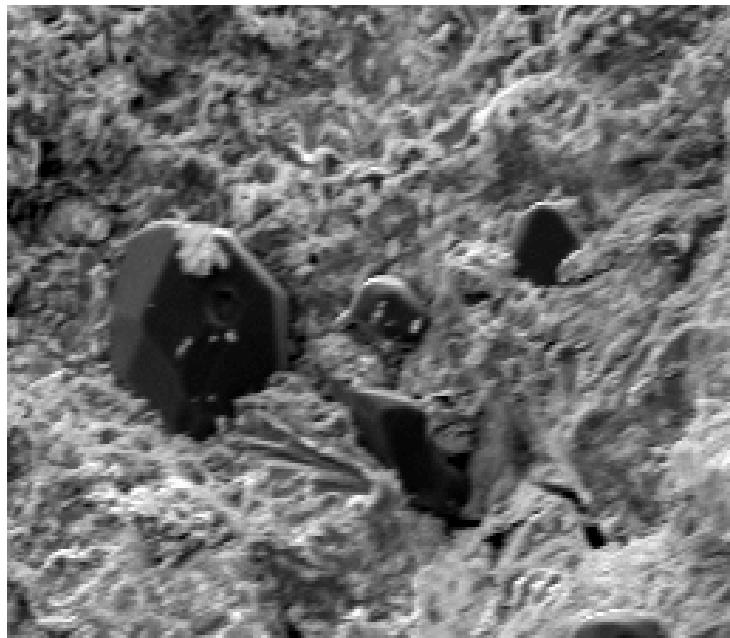


Figure 7. Elemental mapping of cross section of sample DL00046 by electron microprobe (240X).

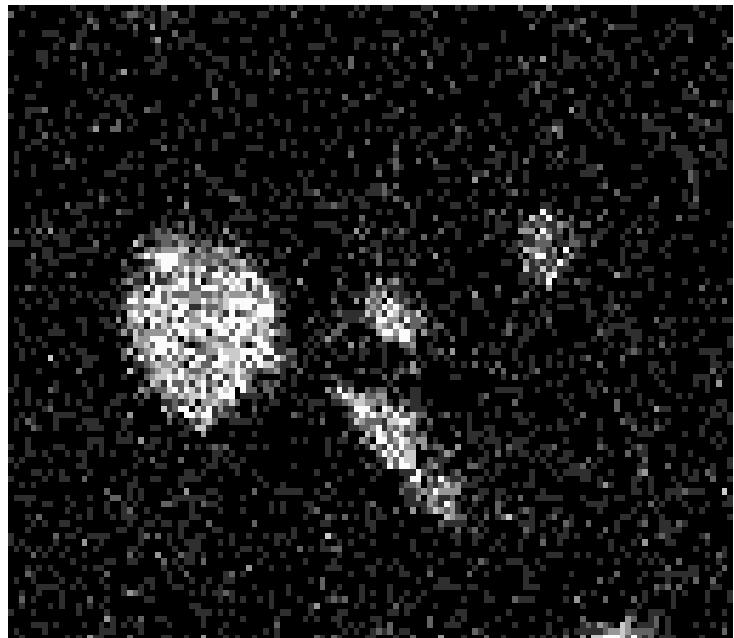


# Elemental Mapping

## SEM-EDS



crystals



sulfur mapping



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# Sulfur Speciation in Scale

Sample	FeS, %S	FeS <sub>2</sub> , %S	Native S, %S	SO <sub>4</sub> , %S	XRF S, %S
Site 1- Pipe 1	<0.005	0.044	0.926	NA	2.66
Site 1- Pipe 2	0.038	0.78	0.066	0.064	1.02
Site 2- Pipe1a	<0.005	11.0	NA	0.399	20.9
Site 2- Pipe1c	0.045	0.421	7.72	NA	9.09
Site 2- Pipe1d	0.056	7.77	NA	0.471	13.7



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# Mineralogy

## XRD

Sample/Layer	Highly Likely	Likely
A1	calcite, goethite, lepidocrocite, magnetite	
A2	calcite, goethite, lepidocrocite, magnetite	sulfur
dl00038	goethite, lepidocrocite, siderite, sulfur	
dl00039	lepidocrocite, quartz	
dl00042	goethite, lepidocrocite, sulfur	
dl00046a	calcite, goethite, lepidocrocite, marcasite, sulfur	siderite
dl00046b	calcite, goethite, lepidocrocite, sulfur	
dl00046c	calcite, goethite, lepidocrocite, siderite, sulfur	
dl00046d	calcite, goethite, lepidocrocite, quartz, siderite, sulfur	



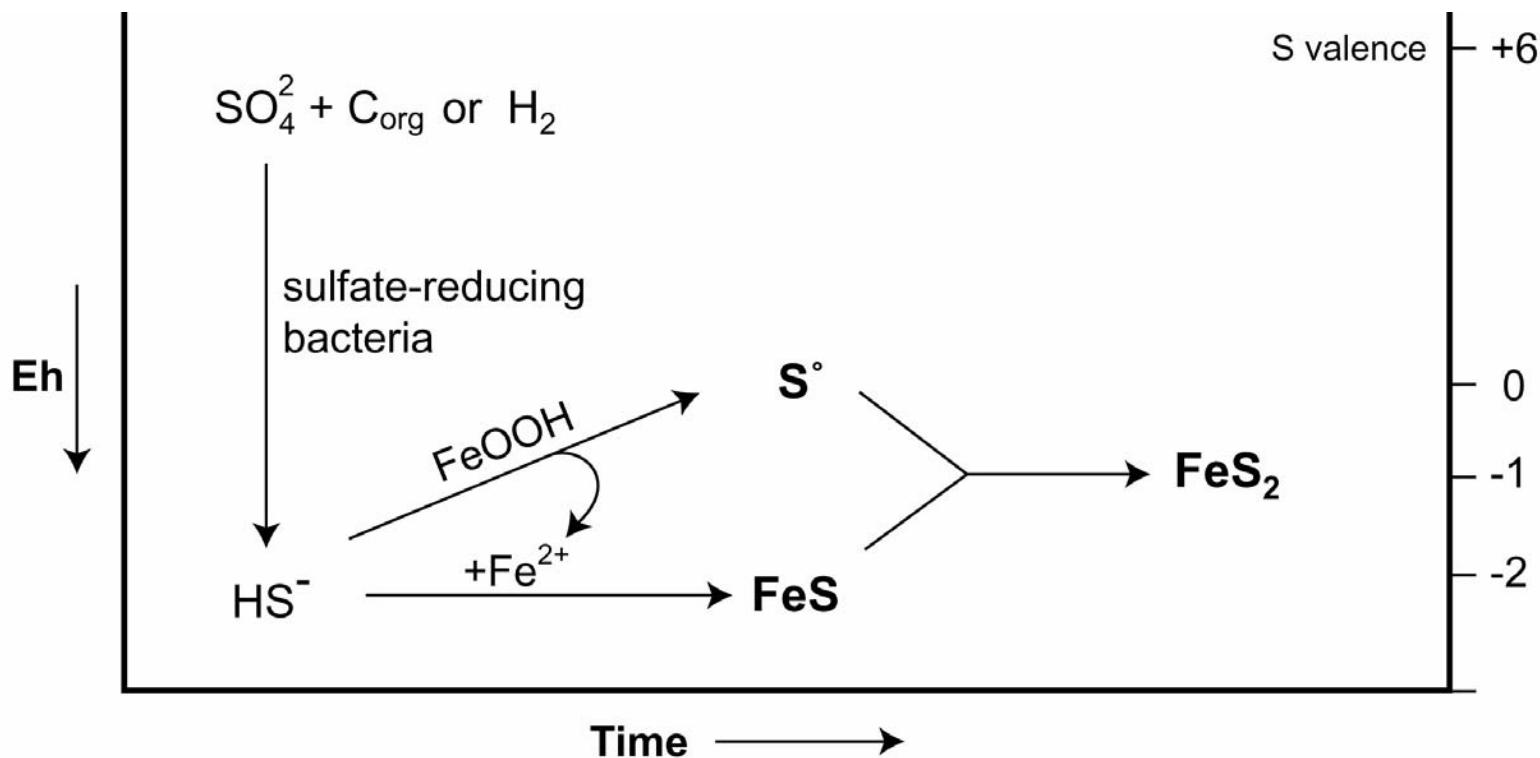
# SRB's



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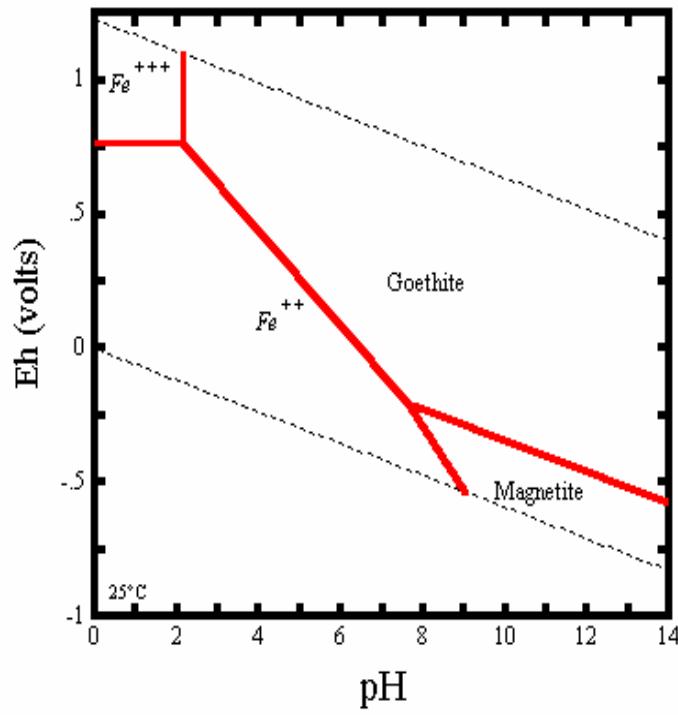
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# Reaction Pathways

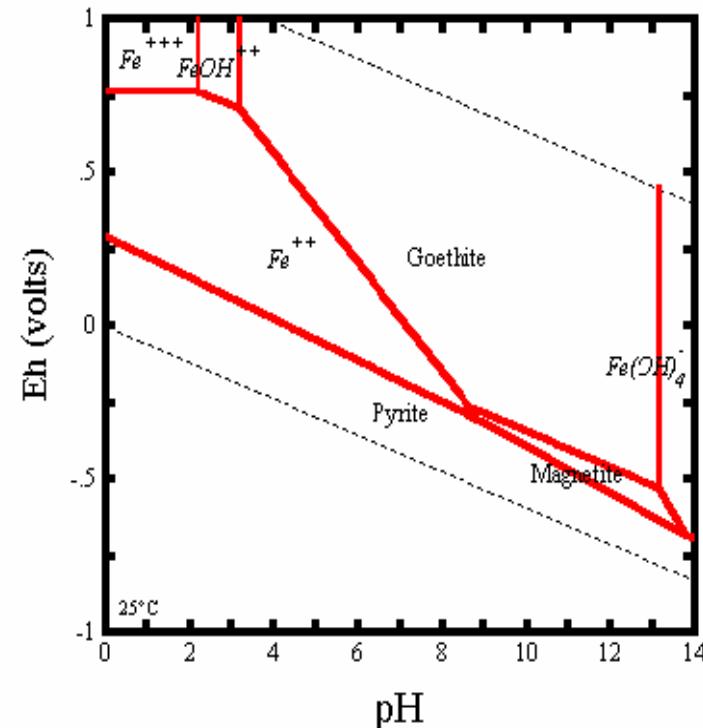


# Eh-pH Diagram for Fe-S-O System

$10^{-6}$  M Fe, 25°C, Geochemists Workbench



0 M Sulfur



$10^{-3}$  M Sulfur



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# Conclusions

- Sulfur was a relatively large component of iron corrosion scales
- Amount of sulfur related to redox conditions
- Sulfur and iron mineralogy was controlled by SRB activity
- SRBs still active in tubercles of well chlorinated tap water

